Impact of aircraft emissions on NO_x in the lowermost stratosphere at northern midlatitudes

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Abstract. Airborne measurements of NO_x, total reactive nitrogen (NO_y), O_3, and condensation nuclei (CN) were made within air traffic corridors over the U.S. and North Atlantic regions (35-60 °N) in the fall of 1997. NO_x and NO_y data obtained in the lowermost stratosphere (LS) were examined using the calculated increase in NO_y (ΔNO_y) along five-day back trajectories as a parameter to identify possible effects of aircraft on reactive nitrogen. It is very likely that aircraft emissions had a significant impact on the NO_x levels in the LS inasmuch as the NO_x mixing ratios at 8.5-12 km were significantly correlated with the independent parameters of aircraft emissions, i.e., ΔNO_y levels and CN values. In order to estimate quantitatively the impact of aircraft emissions on NO_x and CN, the background levels of CN and NO_x at O_3 = 100-200 ppbv were derived from the correlations of these quantities with ΔNO_y. On average, the aircraft emissions are estimated to have increased the NO_x and CN values by 130 pptv and 400 STP cm^{-3}, respectively, which corresponds to 70±30 % and 30±20 % of the observed median values.

Introduction

Active nitrogen ($NO_x = NO + NO_2$) plays a crucial role in the photochemistry of ozone in the upper troposphere (UT) and lowermost stratosphere (LS) [*Singh et al.*, this issue; *Jaeglé et al.*, this issue]. The LS is the region bounded by the extratropical tropopause and 385 K isentrope that generally corresponds to the potential temperature at the tropical tropopause [*Holton et al.*, 1995]. Major sources of NO_x in the UT are convective transport of NO_x from the lower troposphere, production by lightning, emissions from aircraft, and transport from the stratosphere. Aircraft emissions can be more important in determining NO_x levels in the LS than in the UT since the transport of tropospheric NO_x into the stratosphere is quite limited. However, the impact of aircraft on large-scale distribution of NO_x in the LS is still poorly known. Meridional distributions of NO_x and NO_y at latitudes between 40-90 °N were measured in the LS mostly in winter on board the DC-8 during the Airborne Arctic Stratospheric Expedition (AASE) I [*Carroll et al.*, 1990] and II [*Weinheimer et al.*, 1994; *Witte et al.*, 1997]. Decreases in the NO_x mixing ratios from 40 °N to the polar region were observed. Aircraft measurements of NO_x, CN, and other trace species were made inside and outside aircraft plumes over the North Atlantic [e.g., *Schumann et al.*, 1995; *Schlager et al.*, 1997]. During the SASS Ozone and NO_x Experiment (SONEX), reactive nitrogen and a number of tracers were measured in the North Atlantic Flight Corridor (NAFC) region, where NO_x emissions from commercial aircraft are believed to be the greatest [*Singh et al.*, this issue]. The purpose of this study was to understand the effect of aircraft on NO_x in the LS over these regions.

Aircraft Data

The mixing ratios of NO, NO_x, NO_y, O_3, CO, H_2O, and CN obtained during SONEX were the key parameters used for the present analysis. Assuming the photostationary state, the NO_2 values were calculated using the mixing ratios of NO and O_3, and the NO_2 photolysis rates observed at solar zenith angles lower than 87°. The uncertainties in the NO_2 and NO_x values above 7 km were about ±30 and ±10 %, respectively.

Concentrations of total CN and nonvolatile CN with diameters larger than 15 nm were measured with a precision of ±10 % using the two separate CN counters as described in *Anderson et al.* [1998a, 1998b]. The observed concentrations in number of particles cm^{-3} at an ambient pressure and temperature were normalized to number per STP cm^3 (0 °C and 1013 hPa) to represent the CN mixing ratio.

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Results and Discussion

The aircraft measurements in the NAFC region showed simultaneous enhancements in the NO_y and CN levels lasting from a few seconds to 100 seconds. On 252 occasions, NO_y enhancements exceeding 100 pptv above the background levels were identified as being due to aircraft emissions in the UT and the LS [Anderson et al., this issue]. The median duration of the NO_y and CN enhancements was 13 seconds, corresponding to an aircraft plume with a width of 3 km. These spike data were excluded from the analysis described below, although the screening of the data did not alter the statistical results. A dynamical simulation has shown that aircraft plumes disperse to be about 4 km wide an hour after emission [Schumann et al., 1995]. This means that plumes that have existed less than several hours were excluded from the present analysis. In the present analysis, we used the LS data obtained between 310 and 360 K potential temperature (0-2 km above the tropopause) over the U.S. and North Atlantic regions (35-60 °N) with $O_3 >$ 100 ppbv. Associated with the tropopause folding, air masses with $O_3 > 100$ ppbv were transported well below the tropopause height, which was determined from the temperature and O_3 profiles obtained by the Microwave Temperature Profiler (MTP) and UV lidar (DIAL). These data were also excluded.

The median NO_x mixing ratio increased with the increase in the median O_3 mixing ratio where $25 < O_3 < 125$ ppbv. The median NO_x value at $O_3 = 125$ ppbv was 3.5 times larger than that at $O_3 = 25$ ppbv. The increase in the median NO_x mixing ratios in this O_3 range was associated with a corresponding increase in the median NO_y values, resulting in nearly constant NO_x/NO_y ratios of 0.25. By contrast, the median NO_y values increased by only 15 % (50 %) with the increase in the median O_3 mixing ratio where $100 < O_3 < 200$ ppbv ($200 < O_3 < 350$ ppbv). Accordingly, the changes in the NO_x mixing ratios were reflected directly in the NO_x/NO_y ratios in the LS. The median NO_x levels decreased with the increase in O_3 where $O_3 > 200$ ppbv. Given the NO_x

dependence on O_3, the analysis below was made for the two ranges, $100 < O_3 < 200$ ppbv and $200 < O_3 < 350$ ppbv. Where $O_3 > 100$ ppbv, the CO mixing ratios were mostly lower than 70 ppbv, indicating that the LS air was not significantly influenced by highly polluted tropospheric air.

Figure 1a shows the profiles of the 10-second averaged values of NO_x obtained in the LS, together with the median values for each 1 km step. In this figure two profiles for the different O_3 ranges are given. At 8.5-11.5 km, the NO_x mixing ratios often showed large enhancements from the median values. The median NO_x values above 10 km were higher than those below 8 km by a factor of 4 where $100 < O_3 < 200$ ppbv. Similar to the NO_x mixing ratios, the CN mixing ratios above 10 km (not shown) were larger than those below 8 km by a factor of 2. Inasmuch as commercial air traffic was the busiest between 10 km and 12 km [*Gardner*, 1998], the increases in the NO_x and CN mixing ratios at these altitudes suggest the influence of aircraft on these species.

In order to understand the impact of air traffic on the variability of the NO_x levels more quantitatively, increases in the NO_x mixing ratios along five-day kinematic back trajectories were calculated by integrating the NO_x molecules emitted from aircraft into these air masses. For this calculation, the monthly mean NO_x emission distribution from the ANCAT/EC2 emissions inventory [*Gardner*, 1998] was used. Diurnal variations in emissions were not taken into account. The ANCAT/EC2 1992 NO_x emission values were multiplied by 1.17 to account for the increase between 1992 and 1997 [*Brasseur et al.*, 1998]. The time step of the calculation was one hour and the typical NO_x emission rate in the corridor region was 2-5 pptv/hour. The total increase in the calculated NO_x abundance assuming no chemical or diffusional losses represents the increase in NO_y and therefore is denoted as ΔNO_y. A similar method but including chemistry along the back trajectories was applied to the NO_x and NO_y data obtained during AASE II [*Witte et al.*, 1997].

The ΔNO_y profiles are shown in Figure 1b. Where $100 < O_3 < 200$ ppbv, the ΔNO_y values above 10 km were significantly higher than those below, consistent with the NO_x and CN profiles. The median ΔNO_y value at 10-12 km was about 150 pptv, which represents a significant portion of the NO_x value observed at the same altitudes. The ΔNO_y values where $200 < O_3 < 350$ ppbv were lower than those where $100 < O_3 < 200$ ppbv by a factor of about 2, although the cause of the ΔNO_y dependence on O_3 is not understood. Therefore the O_3 dependence of the ΔNO_y values partly explains the dependence of the NO_x values on the O_3 values.

The observed values of NO_x and CN are directly compared with ΔNO_y in Figure 2. For this comparison, data obtained between 8.5 and 12 km were used. The NO_x and CN mixing ratios increased with ΔNO_y, expressed by the following equations:

$$[NO_x] = 58 + 1.026[\Delta NO_y] \qquad (r^2 = 0.50) \qquad (1)$$

$$[CN] = 1022 + 4.17\,[\Delta NO_y] \qquad (r^2 = 0.23) \qquad (2)$$

Here $[NO_x]$ and $[\Delta NO_y]$ are expressed in units of pptv and [CN] is expressed in the unit of number STP cm^{-3}. The square of the correlation coefficient is given as r^2. The number of days the air mass took to reach 50 % of the ΔNO_y values is also indicated in Figure 2. It can be seen that the injection of NO_y occurred rather uniformly over the five-day period. For the ΔNO_y values of 120-170 pptv with the most recent aircraft injections, the effect of chemical loss of NO_x should be at a minimum. Even for this data, the scatter in the observed NO_x values ranged from 100 to 300 pptv, partly due to a neglect of diurnal variations of the NO_x emissions in estimating the ΔNO_y values from the ANCAT/EC2 inventory. The slope in equation (1) is close to 1, suggesting that a

significant portion of ΔNO_y remained in the form of NO_x.

In addition to ΔNO_y, the CN mixing ratio also serves as a parameter by which to characterize the degree of the effect of aircraft on NO_x. It is free from the uncertainty in the emission inventory associated with the ΔNO_y estimate since NO_x and CN are emitted from aircraft simultaneously. First, the relationship between enhanced levels of NO_y (δNO_y) and CN (δCN) in aircraft plumes was derived. The $\delta NO_y/\delta CN$ ratios were scattered between 0.04 and 0.2 and the median value was 0.11 pptv cm^3. The wide range in the $\delta NO_y/\delta CN$ ratios reflects the variability in the emission indices (EI's) of CN and NO_2, depending on various parameters, including the type of the engine, sulfur content in the fuel, and fuel flow [*Anderson et al*, 1998a and 1998b; *Kärcher et al.*, 1998]. Assuming an NO_2 EI of 11 g/kg (fuel burned), the $\delta NO_y/\delta CN$ ratio of 0.11 pptv cm^3 corresponds to a CN EI of 4.8×10^{16} particles/kg (fuel burned). This value falls within the range of the values obtained by the aircraft measurements during SUbsonic aircraft: Contrails and Cloud Effects Special Study (SUCCESS) [*Anderson et al*, 1998a and 1998b].

The 10 s averaged values of NO_x obtained above 8.5 km where $100 < O_3 < 200$ ppbv are plotted versus the CN mixing ratios in Figure 3. For comparison, the median relationship of $\delta NO_y/\delta CN = 0.11$ pptv cm^3 is also shown. The NO_x values were positively correlated with the CN mixing ratio. In addition, the average relationship between NO_x and CN was close to that observed in aircraft plumes.

Aircraft engines were observed to emit volatile particles much more abundantly than nonvolatile particles [*Anderson et al.*, 1998a, 1998b; *Kärcher et al.*, 1998]. The NO_x mixing ratios are plotted versus the ratios of concentrations of nonvolatile to total CN (nonvolatile/total CN) in Figure 4. For comparison, the median δNO_y values in the

aircraft plumes observed during SONEX, including those from DC-8, are plotted versus the nonvolatile/total CN ratios of 0.05 ± 0.05 and 0.15 ± 0.05, respectively. The NO_x values are anti-correlated with the nonvolatile/total CN ratio. The nonvolatile/total CN ratio was 0.2 where $[NO_x] = 200$ pptv increasing to 0.4 ± 0.1 where $[NO_x] = 80$ pptv. It is also seen that the nonvolatile/total CN ratios higher than 0.4 were dominated by air masses with $[\Delta NO_y] < 100$ pptv. In the aircraft plumes, the δNO_y values also decreased with the increase in the nonvolatile/total CN ratios. These values are close to those extrapolated from the non-plume data.

The similarity in the NO_x-CN correlation in the LS air and aircraft plumes was caused by the similarity in the lifetimes of NO_x and CN. The diel steady state model [*Jaeglé et al.*, this issue] predicts that after being emitted from aircraft at 10 km, NO_x was oxidized to higher-oxide nitrogen, primarily to HNO_3, with a time constant of about 2-4 days in the $100 < O_3 < 200$ ppbv region, depending on latitudes, O_3 values, and aerosol surface area. On the other hand, CN is lost primarily through coagulation with CN for $[CN] > 500$ cm^{-3}. The half-lifetime of CN with a diameter of 15 nm at $[CN] = 1000$ cm^{-3} is 3-4 days and decreases inversely in the CN mixing ratio [*Pruppacher and Klett*, 1997]. The NO_x and CN are transported from the LS to the troposphere, limiting the ultimate age of the aircraft-affected air.

NO_x has sources in the troposphere other than emissions from aircraft as discussed in the introduction. Similarly, CN is also produced in the troposphere by processes including condensation of sulfuric acid. In fact, during SONEX, the NO_x and CN mixing ratios were strongly enhanced in the tropospheric air masses impacted by lightning and convection as observed on November 9, 1997. In addition to aircraft emissions, the mixing of tropospheric air high in NO_x and CN into the stratosphere might have contributed to the positive NO_x-CN correlation. However, it is unlikely that this

process had a pronounced effect on the observed correlations given that the NO_x mixing ratios failed to show significant correlation with either the CO or H_2O mixing ratios (not shown). Similarly, CN did not show significant correlation with either CO or H_2O. In turn, the CO and H_2O mixing ratios observed during SONEX generally decreased with the O_3 mixing ratios as expected from the tropospheric-stratospheric exchange. The effect of aircraft emissions on CO in the LS and troposphere is negligibly small according to the CO EI of 1-10 g/kg estimated by *Baughcum et al.* [1998]. Therefore, it is unlikely that the enhanced levels of NO_x and CN in the LS were primarily caused by transport of these species from the troposphere.

The increase in the NO_x values due to aircraft exhaust can be estimated using two independent parameters which characterize the impact of aircraft emissions: ΔNO_y and CN mixing ratios. From equations (1) and (2), the background values of CN and NO_x where $100 < O_3 < 200$ ppbv are defined as 1022 ± 322 cm^{-3} and 58 ± 45 pptv, respectively, as the values for $[\Delta NO_y] = 0$. On the other hand, the median NO_x value where [CN] was lowest (500-1000 cm^{-3}) were 68 ± 28 pptv, which is close to the background value determined from equation (1). The median and average values of CN and NO_x are summarized in Table 1, together with the background values. Based on these values, we estimated the aircraft emissions to have increased on average, the values of CN and NO_x by 411 cm^{-3} and 133 pptv, respectively. These values correspond to 30 ± 23 % and 70 ± 27 % of the median observed CN and NO_x values, respectively.

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Figure captions

Figure 1. Profiles of the NO_x and ΔNO_y values for air masses where $100 < O_3 < 200$ ppbv and $200 < O_3 < 350$ ppbv. The ΔNO_y values are the calculated increases in NO_y along five-day back trajectories. The median values at each 1 km step are also shown. The bars indicate central 67 % values.

Figure 2. NO_x and CN mixing ratios plotted versus ΔNO_y above 8.5 km. Where $100 < O_3 < 200$ ppbv, the data points are classified according to the time (T) required to increase the ΔNO_y values by 50 %. $0 < T < 1$ day (closed circles), $1 < T < 2$ days (open circles), and $3 < T < 5$ days (crosses).

Figure 3. NO_x mixing ratio plotted versus CN mixing ratios observed above 8.5 km (closed circles). The least square fitted line is shown as a solid line. The median NO_x-CN relationship obtained from aircraft exhaust plumes is shown as a dashed line.

Figure 4. NO_x mixing ratios plotted versus the nonvolatile/total CN ratios. The points where $\Delta NO_y > 100$ pptv and $\Delta NO_y < 100$ pptv are shown as closed circles and open circles, respectively. The median values obtained from aircraft exhaust plumes observed during SONEX are shown as large closed circles.

Table 1. Background (BG), median (MED), and average values of CN and NO_x observed above 8.5 km where $100 < O_3 < 200$ ppbv. The uncertainties in the background values were defined as the 1-σ standard deviation of the differences between the observed values and those calculated from equations (1) and (3) where $\Delta NO_y < 50$ pptv.

	CN (cm^{-3})	NO_x (pptv)
BG	1022 ± 322	58 ± 45
MED	1433	191
Average $\pm$ 1σ	1500 ± 502	178 ± 70
MED–BG	411	133
(MED–BG)/MED	29 %	70 %

Altitude (km)

NO_x (pptv)

ΔNO_y (pptv)

(a)

(b)

- $100 < O_3 < 200$ ppbv
○ $200 < O_3 < 350$ ppbv

Above 8.5 km
$100 < O_3 < 200$ ppbv

● age < 1 day
○ age < 2 day
+ age < 5 day
—— $r^2 = 0.23$

Above 8.5 km
$100 < O_3 < 200$ ppbv

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